

CONTININOUS TIME-OF-FLIGHT ION MASS SPECTROMETER

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FIELD OF THE INVENTION

10 The present invention generally relates to mass spectrometers, and, more specifically, relates to a time-of-flight ion mass spectrometer that can operate continuously. This invention was made with Government support under Contract No. W-7405-ENG-36 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

15 **BACKGROUND OF THE INVENTION**

Mass spectrometers are used extensively in the scientific community to measure and analyze the chemical compositions of substances. In general, a mass spectrometer is made up of a source of ions that are used to ionize neutral atoms or molecules from a solid, liquid or gaseous substance, a mass analyzer 20 that separates the ions in space or time according to their mass or their mass-per-charge ratio, and a detector. Several variations of mass spectrometers are available, such as magnetic sector mass spectrometers, quadrupole mass spectrometers, and time-of-flight mass spectrometers.

25 The magnetic sector mass spectrometer uses a magnetic field or combined magnetic and electrostatic fields to measure the ion mass-per-charge ratio. In one type of magnetic sector geometry, {see A.O. Nier, *Review of Scientific Instruments*, Vol. 18 (1947) p. 398; L. Holmlid, *International Journal of Mass Spectrometry and Ion Physics*, Vol. 17 (1975) p. 403} only one mass-per-charge species is detected at any one time, so the magnetic field strength and, if 30 present, the electric field strength must be varied in order to obtain a mass spectrum comprising multiple mass-per-charge species. Major limitations on this type of mass spectrometer are the high mass of the magnet and the time that is required to scan the entire mass range one mass at a time.

35 Another type of magnetic sector mass spectrometer creates a monoenergetic beam of ions, which are spatially dispersed according to mass-per-charge ratio, and which are focused onto an imaging plate {e.g., J. Mattauch and R. Herzog, *Zeitschrift fur Physik*, Vol. 89 (1934) p. 786}. While this type of

- 5 and R. Herzog, *Zeitschrift fur Physik*, Vol. 89 (1934) p. 786}. While this type of spectrometer can detect multiple mass-per-charge species can be detected simultaneously, the poor spatial resolution it provides limits its use to a narrow mass range.

Quadrupole mass spectrometers utilize a mass filter having dynamic electric fields between four electrodes {e.g., Quadrupole Mass Spectrometer and its Applications, ed. Peter H. Dawson (American Institute of Physics, New York, 1995)}. These fields are tailored to allow only one mass-per-charge ion to pass through the filter at a time. Major limitations of quadrupole mass spectrometers are the high mass of mass of the required magnet and the time required to scan the entire mass range one mass at a time.

Time-of-flight mass spectrometers (TOFMS) can detect ions over a wide mass range simultaneously {see W.C. Wiley and I.H. McLaren, *Rev. Sci. Instrum.*, Vol. 26 (1955) p. 1150; M. Guilhaus, *J. Mass Spectrom.*, Vol. 30 (1995) p. 1519}. Mass spectra are derived by measuring the times for individual ions to traverse a known distance through an electrostatic field free region. In general, the mass of an ion is derived in TOFMS by measurement or knowledge of the energy, E, of an ion, measurement of the time, t_1 , that an ion passes a fixed point in space, P_1 , and measurement of the later time, t_2 , that the ion passes a second point, P_2 , in space located a distance, d, from P_1 . Using an ion beam of known energy-per-charge E/q , the time-of-flight (TOF) of the ion is $t_{TOF} = t_2 - t_1$, and by the ion speed is $v = d/t_{TOF}$. Since $E = 0.5 mv^2$, the ion mass-per-charge m/q is represented by the following equation:

$$\frac{m}{q} = \frac{2Et_{TOF}^2}{qd^2} . \quad 10$$

The mass-per-charge resolution, commonly referred to as the mass resolving power of a mass spectrometer, is defined as:

$$\frac{\Delta m/q}{m/q} = \frac{\Delta E}{E} + 2\frac{\Delta t_{TOF}}{t_{TOF}} + 2\frac{\Delta d}{d} , \quad 11$$

- 5 where ΔE , Δt_{TOF} , and Δd are the uncertainties in the knowledge or measurement of the ion's energy, E , time-of-flight, t_{TOF} , and distance of travel, d , respectively, in conventional time-of-flight spectrometers.

In a gated TOFMS in which a narrow bunch of ions is periodically injected into the drift region, uncertainty in t_{TOF} may result, for example, from ambiguity in
10 the exact time that an ion entered the drift region due to the finite time, Δt_1 , that the gate is "open," i.e. $\Delta t_1 \approx \Delta t_{TOF}$. The ratio of $\Delta t_{TOF}/t_{TOF}$ can be minimized by decreasing Δt_{TOF} , for example, by decreasing the time the gate is "open." This ratio can also be minimized by increasing t_{TOF} , for example, by increasing the distance, d , that an ion travels in the drift region. Often, a reflectron device is
15 used to increase the distance of travel without increasing the physical size of the drift region.

Uncertainty in the distance of travel, d , can arise if the ion beam has a slight angular divergence so that ions travel slightly different paths, and, therefore, slightly different distances to the detector. The ratio of $\Delta d/d$ can be
20 minimized by employing a long drift region, a small detector, and a highly collimated ion beam.

The uncertainty in the ion energy, E , may result from the initial spread of energies, ΔE , of ions emitted from the ion source. Therefore, ions are typically accelerated to an energy, E , that is much greater than ΔE .

25 A further limitation of conventional mass spectrometry lies in the fact that the source of ions is a separate component from the time-of-flight section of a spectrometer, and it requires significant resources. First, most ion sources are inherently inefficient, so that few atoms or molecules of a gaseous sample are ionized, thereby requiring a large volume of sample and, in order to maintain a
30 proper vacuum, a large vacuum pumping capacity. Second, the ion source typically generates a continuous ion beam that is gated periodically, creating an inefficient condition in which sample material and electrical energy are wasted during the time the gate is "closed." Third, ions have to be transported from the ion source to the time-of-flight section, requiring, among other things,

5 electrostatic acceleration, steering and focusing. Fourth, typical ion sources introduce a significant spread in energy of the ions so that the ions must be substantially accelerated to minimize the effect of this energy spread on the mass resolving power. Finally, having an ion source separate from the drift region creates an apparatus having large mass and volume.

10 Still another problem with conventional time-of-flight mass spectrometers is that ions must be localized in space at time t_1 in order to minimize Δd and therefore, minimize the mass resolving power. Typically, time t_1 corresponds to the time that the ion is located at the entrance to the drift region.

15 In addition to these limitations that impact the mass resolving power of prior art TOFMS, an important further limitation is the intrinsically low duty cycle associated with the gating process in which a group of ions briefly is admitted at time t_1 into the drift region. The time that must elapse before another group of ions can be admitted is determined by the time required for the heaviest, and therefore the slowest, ion, admitted at time t_1 , to reach the detector. This
20 generally long period is necessary to prevent overlap of mass spectra, which are accumulated each gating period. Although sophisticated techniques have been developed in attempts to improve this limitation, the duty cycle of prior art TOFMS is still much less than unity.

One method of attempting overcome this limitation in TOFMS utilizes a
25 thin foil located at the entrance to the drift region. A sample ion having sufficient energy to traverse the foil will continue to the "stop" detector. Secondary electrons generated by the interaction of the sample ion with the foil are detected, and provide a measurement of the time t_1 that the ion entered the drift region. However, this method is not without its own limitations. These limitations
30 include the requirement that the incident ion have sufficient energy to transit the foil, the energy degradation of the sample ion due to interaction with the foil, and the angular scattering of the sample ion due also to its interaction with the foil.

The present invention solves these problems of the prior art by continuously ionizing sample atoms or molecules that are initially at rest inside a

- 5 drift region having an electric field. The secondary electron that is created by the ionization event is detected to provide the time t_1 , and the detection of the ion at a "stop" detector provides the stop time t_2 .

SUMMARY OF THE INVENTION

In order to achieve the objects and purposes of the present invention, and
10 in accordance with its objectives, a time-of-flight ion mass spectrometer
comprises an evacuated enclosure, with means for generating an electric field
located in the evacuated enclosure, and means for injecting a sample
material into the electric field. A source of continuous ionizing radiation
injects ionizing radiation into the electric field to ionize atoms or molecules of
15 the sample material, and timing means for determining time elapsed between
arrival of a secondary electron having a particular energy out of the ionized
atoms or molecules at a first predetermined location and arrival of a sample
ion having a particular energy out of the ionized atoms or molecules at a
second predetermined location.

20

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawing, which is incorporated in and forms a part of
the specification, illustrates an embodiment of the present invention and, together
with the description, serves to explain the principles of the invention. In the
25 drawing:

FIGURE 1 is a schematic illustration of an embodiment of the present
invention showing the elements of the invention and its operation with a static
electric field.

FIGURE 2 is a schematic illustration of another embodiment of the present
30 invention in which one method of introducing a linear electric field.

FIGURE 3 is a schematic illustration of still another embodiment of the
present invention in which a thin foil is installed at each end of the drift region.

5 FIGURE 4 is a schematic illustration of still another embodiment of the present invention in which the energy of the secondary electron and the energy of the ion are measured.

DETAILED DESCRIPTION

The present invention continuously ionizes sample atoms or molecules
 10 within a drift region having an electric field of magnitude $\epsilon(z)$, aligned coaxially with the central z-axis of a drift region. The electric field accelerates the secondary electrons toward a first detector, and the generated ions toward a second detector. The invention provides high mass resolving power, smaller resource requirements in such areas as mass, power, volume, and pumping
 15 capacity, a high efficiency, since nearly every ionization event is detected, and elimination of the prior art requirement that the location of an ion at time t_1 must be known in order to measure its time-of-flight in the drift region. The invention can be understood more easily through reference to the drawing.

Referring to Figure 1, there can be seen the time-of-flight mass
 20 spectrometer 10 of the present invention resides inside evacuated chamber 11. The gaseous sample to be investigated is introduced into drift region 12 by sample inlet 13. Alternatively, a solid sample could be introduced, for example, at the surface of an electrode placed in drift region 12. As shown, a static electric field exists between start detector 17 and stop detector 16 due to the difference
 25 in voltage between V_1 and V_2 , with V_1 being negative with respect to V_2 .

The general equation governing the motion of an ion in a static electric field is:

$$m \frac{d^2 z}{dt^2} = q\epsilon(z) , \quad 12$$

which can be solved analytically or numerically depending on the functional form
 30 of $\epsilon(z)$. For a sample ion initially at rest, the solution of Equation 11 provides the mass-per-charge of the sample ion if the time-of-flight, t_{TOF} , distance of travel, d , and electric field, $\epsilon(z)$, are known.

- 5 If the electric field created by the difference in potential between V₁ and V₂ is constant across the drift region, as it is in one embodiment of the present invention (i.e., ε(z) = ε₀), and the ionization event occurs at a known distance from stop detector 16, the mass-per-charge of an ion initially at rest is:

$$t_{TOF} = \left(\frac{2md}{q\epsilon_0} \right)^{1/2} \quad 13$$

- 10 Under the initial conditions that stop detector 16 is located at z = 0, and that the ion is created at rest at a distance of z = d from stop detector 16, the time-of-flight of the ion according to Equation 12 is:

$$\frac{m}{q} = \frac{\epsilon_0 t_{TOF}^2}{2d} \quad 14$$

- 15 Knowledge of the distance of travel, d, generally requires that the ionization event occur at a fixed, known distance from stop detector 16. This can be achieved by using a continuous ionizing radiation source 19 whose ionizing particles are confined to a thin plane having a thickness, g, oriented perpendicular to the z-axis. However, the mass resolving power of the present invention is dependent on g/d, which can be minimized by minimizing g.

- 20 Continuous ionizing radiation source 19 ionizes sample atoms or molecules and creates a secondary electron that is accelerated to start detector where it is detected at time, t₁. The ionized atom or molecule also is accelerated by the electric field, but toward stop detector 16, where the ionized atom or molecule is detected at time, t₂. The time-of-flight of the secondary electron from the ionization event to the start detection is much shorter than the time-of-flight of the ion from the ionization event to the stop detector, so the difference in times, t₂ – t₁, corresponds to the time-of-flight of the ionized atom or molecule over the distance that it travels from the time it was ionized to the time it is detected at stop detector 16.

- 25 30 An ionized sample atom or molecule is considered to be initially at rest in the z direction if its initial energy in the z-direction is much less than the energy to which the ion is accelerated in drift region 12. It is well known to those having

5 skill in this art, that the mean kinetic energy of a gaseous atom or molecule is $1.5 kT$, where k is the Boltzman constant, and T is the temperature of the gas. At room temperature (approximately 300 K), the mean energy is approximately 0.04 eV. Therefore, an ionized sample atom or molecule can be at rest if the energy to which it is accelerated by the linear electric field in drift region **12** is much
10 greater approximately 0.04 eV. For example, a typical acceleration by the electric field would be several kilovolts, so an ion can be considered to initially at rest.

Another embodiment of the present invention utilizes an electric field that linearly increases in magnitude along the z-axis in drift region **12** from stop detector **16** to start detector **17**, as is shown in Figure 2. In this embodiment, the electric field is defined by $\epsilon(z) = kz$, where k is a constant that depends only on the electromechanical configuration of drift region **12**. Assuming that a sample ion starts from a rest condition in drift region **12**, the solution of Equation 12 using this electric field will yield the time-of-flight (and therefore the mass-per-charge)
15 of a sample ion that is independent of the distance of travel, d , of the sample ion in drift region **12**. This eliminates the requirement that continuous ionizing radiation source **19** emit ionizing radiation that is confined to a plane perpendicular to the z-axis, and allows the ionizing radiation to be spatially broad
20 in the z-direction.

25 In this embodiment of the present invention, concentric electrically conductive rings **14** surround drift region **12**, and are connected to resistors **15** that are connected between voltage V_1 and voltage V_2 , as shown, again with V_1 negative with respect to V_2 . Also as shown, V_1 is connected to stop detector **16**, and V_2 is connected to start detector **17** at the opposite end of drift region **12**.
30 This arrangement provides the electric field in drift region **12** that is required by this embodiment of the present invention. The values of resistors **15** are selected to generate the linear electric field along the central axis of drift region **12**. Generally, the values of resistors **15** increase quadratically from stop

5 detector **16** (V_1) to start detector **17** (V_2) for the case of a cylindrical drift region
12.

The electric field created by V_1 and V_2 across resistors **15** and concentric rings **14** is coaxial about central axis **18** (the z axis), and has a magnitude, $\epsilon(z)$, normal to stop detector **16**, as shown in U.S. Patent No.

10 5,168,158, issued December, 1992, to McComas et al. Although concentric rings **14** and resistors **15** effectively provide the electric field for this embodiment of the present invention using a linear electric field, other methods can be used. For example, a dielectric cylinder could surround drift region **12**, and have a resistive coating applied whose resistance varies with the distance from stop detector **16**.
15 Another electric field arrangement could involve appropriately shaped grids at stop detector **16** (V_1) and at start detector **17** (V_2) (see D.C. Hamilton et al., New high resolution electrostatic ion mass analyzer using time-of flight, Rev. Sci. Instrum. Vol. 61 (1990) 3104-3106). It is also possible that combinations of these methods could be used. Any method of effectively producing, in this
20 embodiment, a linear electric field within drift region **12** could be used with this embodiment of the present invention.

Another embodiment of the present invention is illustrated in Figure 3, where thin foils **16a** and **17a** are shown in place in front of stop detector **16** and start detector **17**, respectively. Ions and secondary electrons associated with the 25 ionization event pass through foils **16a**, and **17a** to stop detector **16** and to start detector **17**. Thin foils **16a**, **17a** allow the pressure in drift region **12** to be maintained at a higher level than the operating pressure of start detector **16** and stop detector **17**. This pressure differential also allows a greater amount of sample atoms or molecules in drift region **12**, providing a higher ionization probability per ionizing radiation particle from continuous ionization radiation source **19**. It should be noted, however, that the output of sample inlet **13** must be sufficiently low so that the inverse of the ionization rate, which equals the average time between discrete ionization events, is much longer than the time-of-flight of sample ions in drift region **12** in order to reduce the ambiguity introduced
30

- 5 from multiple signals from start detector 17 or stop detector 16 when two or more ions are ionized nearly simultaneously.

Another embodiment of the present invention is illustrated in Figure 4. In this embodiment, the energy of a secondary electron is measured using electrostatic energy analyzer 20. Since an ion and its secondary electron are formed initially at rest, or nearly at rest, and are accelerated through a known electric field, the energy of the electron at start detector 17, and the energy of the ion at stop detector 16 each provide information of the distance in the z-direction that the initial ionization event occurred. Therefore, measurement of the energy of the secondary electron, the energy of the ion, or both the energy of the electron and the energy of the ion allows determination of the distance of travel, d, of the ion from its formation to stop detector 16. Measurement of the electron energy is the preferred embodiment because the time for an electron to traverse the additional path length required for energy measurement is much shorter than, and therefore insignificant relative to, the time-of-flight of the ion.

Measurement of the energy of an ion or electron by electrostatic energy analyzer 20 may be performed by means of a deflector-type electrostatic analyzer or mirror-type electrostatic analyzer {see D. Roy and R.P. Harkness, Reports on Progress in Physics, Vol. 53 (1990) p. 1621} and located as shown near start detector 17. To represent electrostatic energy analyzer 20 in Figure 4, curvilinear plates 20a, 20b are shown connected to biasing voltages V₃ and V₄. If desired, another electrostatic energy analyzer 21 can be located near stop detector 16. As shown, curvilinear plates 21a, 21b connected to biasing voltages V₅ and V₆. According to the desired application of the present invention, either electrostatic energy analyzer 20 or electrostatic energy analyzer 21 could be used singly, or both electrostatic energy analyzer 20 and electrostatic energy analyzer 21 can be used together.

In this embodiment, it is necessary to connect voltages V₁ and V₂ to electrodes 22 and 23, which define an aperture to allow secondary electrons and sample ions to pass through. One important advantage of this embodiment is

- 5 that the ionizing radiation from continuous ionizing radiation source **19** can be spatially broad in the z-direction.

For all embodiments of the present invention, stop detector **16** and start detector **17** can be any effective single particle detectors that can measure the time the sample ion strikes stop detector **16**, and the secondary electron strikes 10 start detector **17** with time accuracy much less the ion's TOF in drift region **12**. Appropriate detectors for stop detector **16** and start detector **17** include 15 microchannel plate detectors or channel electron multiplier detectors that would detect ionized sample atoms or molecules and secondary electrons that have been accelerated through drift region **12**, and output a signal indicating that detection.

Continuous ionizing radiation source **19** emits continuous ionizing radiation into drift region **12** where it ionizes atoms or molecules of the gas sample of interest. Continuous ionizing radiation source **19** can emit any effective ionizing radiation, such as photons, electrons, or ions, and could be a 20 laser, a source of electrons, or a source of ions.

Those with skill in this art recognize that the invention requires a power supply to provide the necessary potential differences required for V_1 and V_2 , where V_2 is biased negatively with respect to V_1 , to produce the necessary electric field, and to power pulsed ionizing radiation source **19**. Additionally, 25 power is required to be provided for the operation of stop detector **16** and start detector **17**.

As has been explained, the present invention ionizes the sample atoms or molecules inside drift region **12**, not in some external ion source. This allows the invention to be inherently compact, allowing the invention to provide TOFMS 30 apparatus that has a small volume and mass, and that requires reduced power resources. The ionization of sample atoms or molecules inside drift region **12** also allows the present invention to accelerate the ions from a condition of near rest independent of the ion's position within drift region **12**. This allows, in one

5 embodiment, use of a spatially broad continuous ionizing radiation source **19** that is efficient and requires little or no steering, collimation or focusing.

In the present invention, the sample ion is formed when the sample atom or molecule is approximately at rest, and the time-of-flight of the sample ion in drift region **12**, in one embodiment, is independent of the location at which the
10 sample ion was formed. Therefore, the mass resolving power of the sample ion is dependent only on the initial ion energy relative to the energy to which it is accelerated and the accuracy of the time-of-flight measurement, which includes, for example, the timing accuracy of the time-of-flight measurement electronics.

The present invention requires only a small volume of sample material
15 because most ions from sample atoms or molecules are detected. This is in contrast to prior art mass spectrometers, where few ions are extracted from the ion source to form an ion beam or ions that are extracted from the ion source and comprise the ion beam are removed from the ion beam by, among other things, collimating slits, and while the gate is "closed." Additionally, due to the smaller
20 volume of the present invention, the pumping requirements for evacuation of evacuated chamber **11** is reduced, allowing use of a smaller vacuum pump.

Finally, the present invention requires lower voltage differences across drift region **12**. Since a sample atom or molecule is ionized while it is at thermal energies of approximately 0.04 eV at 300 K, the calculated mass-per-charge of
25 the ion is dependent on knowledge accuracy of the ion's energy relative to its accelerated energy as it traverses drift region **12**. Because the spread in the initial energies of the sample ions is small, the acceleration voltage (V_1-V_2) does not have to be high. To put this into perspective, it should be noted that prior art linear ion mass spectrometers have energy spreads that typically range from 2
30 eV to 40 eV, which requires acceleration of the sample ions to a high energy in order to remove the uncertainty of the energies of the sample ions. In one embodiment of the present invention, a single applied voltage (except for the signal electronics) could be applied both as the bias for stop detector **16** and start

- 5 detector **17** and for the voltage $V_1 - V_2$ between stop detector **16** and start detector **17**.

The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many 10 modifications and variations are possible in light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various 15 modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.